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J. Phys. IV France **126** (2005) 27–30

DOI: 10.1051/jp4:2005126006

Piezoelectric properties at high temperature in α-quartz materials

O. Cambon[1], J. Haines[1], G. Fraysse[1], D.A. Keen[2] and M.G. Tucker[3]

[1] *Université Montpellier II, Laboratoire de Physicochimie de la Matière Condensée, UMR CNRS 5617, Place E. Bataillon, 34095 Montpellier Cedex 05, France*
[2] *Department of Physics, Oxford University, Clarendon Laboratory, Parks Road, Oxford, OX1 3PU, UK and ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK*
[3] *Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK*

Abstract. The performances of resonators made of α-quartz and $GaPO_4$ are compared based on piezoelectric measurements up to 850°C. Up to now, no explanation was available for the observed decrease in piezoelectric performances well below the phase transition temperature in these materials. Total neutron scattering measurements were used to determine the instantaneous structural disorder as a function of temperature. The losses of piezoelectric properties measured above 700°C for $GaPO_4$ can thus be correlated to an important degree of structural disorder, which is evaluated by various angular distributions. The distribution of the intertetrahedral O-O-O bridging angle values becomes very wide for this material between 700 and 800°C. The relative movement of the tetrahedra can provide an explanation for the observed piezoelectric losses well before the phase transition.

1. INTRODUCTION

α-Quartz is the most widely used single crystal piezoelectric material at the present time. However, its performance is limited for specific applications as components in microbalances, high-temperature pressure sensors or field-test viscometers. Structure-property relationships have been developed for α-quartz homeotypes at ambient temperature [1-5]. The piezoelectric response was found to be a function of the structural distortion of a material with respect to the β-quartz structure type. This distortion can be described in terms of the intertetrahedral bridging angle θ and the tetrahedral tilt angle δ, which is the order parameter for the α–β phase transition (Note [6] that for β-quartz, θ = 153.3°, δ = 0°).

In this study, the piezoelectric response of an α-quartz resonator is compared to that of a $GaPO_4$ resonator up to 850°C. The piezoelectric properties of α-quartz are limited in principle by the α–β phase transition at 573°C [7]. Similarly the piezoelectric properties of $GaPO_4$ should be expected to vanish at the irreversible, reconstructive transition from the α-quartz type structure (θ = 134.6°, δ = 23.3° at 25°C [8]) to a β-cristobalite phase at 933°C [9]. The piezoelectric measurements on a $GaPO_4$ resonator using a bulk acoustic wave vibrational mode are presented here and discussed in relation with preliminary total neutron scattering results. These results show that as in the case of α-quartz [10] a loss of piezoelectric properties occurs prior to the structural phase transition and that this loss can be related to the increased structural disorder found in total neutron scattering experiments.

2. EXPERIMENTAL

The piezoelectric response of the resonators was measured using a Hewlett-Packard 8753A network analyzer. High-temperature experiments were performed in a controlled temperature furnace (±0.5°C) and the temperature measured with a thermocouple. The piezoelectric properties of a resonator can be

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characterized in terms of two quantities, the mechanical quality factor, Q, which is a measure of the quality of the resonator with respect to acoustic attenuation, and the electromechanical coupling coefficient, k. These two properties are defined as follows:

$$Q = 2\pi L f_r / R \tag{1}$$

$$k = \pi/2[(f_a\text{-}f_r)/f_a]^{1/2} \tag{2}$$

where L is the self-inductance and R is the resistance of the resonator. f_r and f_a are the frequencies of resonance and anti-resonance respectively. The mechanical quality factor is very sensitive to structural disorder and defects in the material and characterizes the purity of the spectral signal.

The third harmonic signals at close to 10 MHz of AT (athermal, i.e. –35.15° Y-rotated cut) cut α-quartz resonators (from C-MAC Frequency Products) were used. Electrical contacts between the electrodes on the resonator and its base were made using a high-temperature, silver containing, conducting polyimide resin (Epotecny P200).

AT-cut (-15.9° Y-rotated cut) $GaPO_4$resonators (from Piezocryst GMBH) were studied using the fundamental thickness shear mode. The metallized plate was held in place by two conductive metallic clips on the electrodes producing the electrical excitation of the resonator.

Instantaneous structural disorder was studied by total neutron scattering measurements on $GaPO_4$ powder using the GEM diffractometer at the ISIS spallation source of the Rutherford Appleton Laboratory for a number of temperatures between 20°C and 1030°C. Rietveld refinements were performed using the program GSAS [11]. Three-dimensional structural models were refined using reverse Monte Carlo (RMC) modeling [12]. These models are essentially a 'snapshot' of the disordered structure, and are consistent with the Rietveld refined average structure, the measured pair correlation functions and the local network topology.

3. RESULTS AND DISCUSSION

3.1 Quartz

The QF values obtained above 400°C are characteristic of a poor resonator. It has been known for many decades [13] that the d_{11} piezoelectric constant of α-quartz begins to decrease gradually at temperatures above 200°C. The known, time-averaged structure [6] of α-quartz does not provide an explanation of this behavior, as the order parameter δ only decreases gradually from 16.4° to 13.2°, for example, between 25 and 424°C. The origin of the deterioration of the piezoelectric response in α-quartz is explained by local instantaneous structural disorder, which can be characterized by bond length, bond angle, tilt angle and intertetrahedral O-O-O bridging angle distributions obtained from total neutron scattering

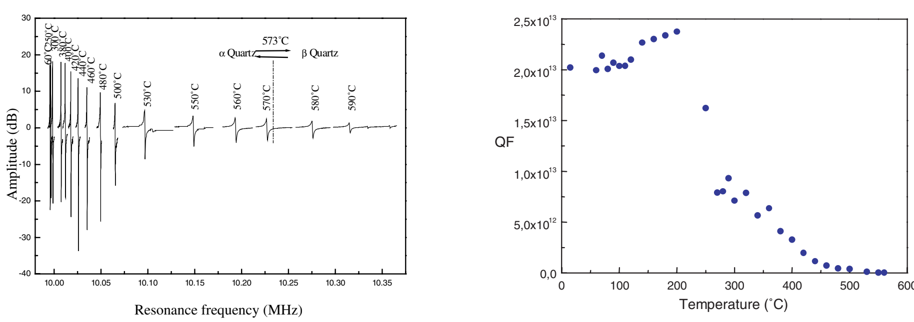

Figure 1. Temperature dependence on the piezoelectric response of an α-quartz resonator.

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measurements [10]. Indeed the Q factor, which is very sensitive to structural disorder and defects, decreases rapidly above 300°C, whereas k, which is more correlated to the static average value [2,3,10] of δ, remains constant.

3.2 $GaPO_4$

Similar behavior has been recorded for gallium orthophosphate (Fig. 2), but at higher temperature because of the very high structural stability of this material [14, 15]. The performance of the piezoelectric resonator (Fig. 2) was good up to 700°C ($QF_{700°C} = 1.0x10^{11}$) and above this temperature the quality of the resonator decreased slowly ($QF_{800°C} = 1.0x10^{10}$). At 850°C, the resonator was of bad quality and the signal disappeared at 900°C.

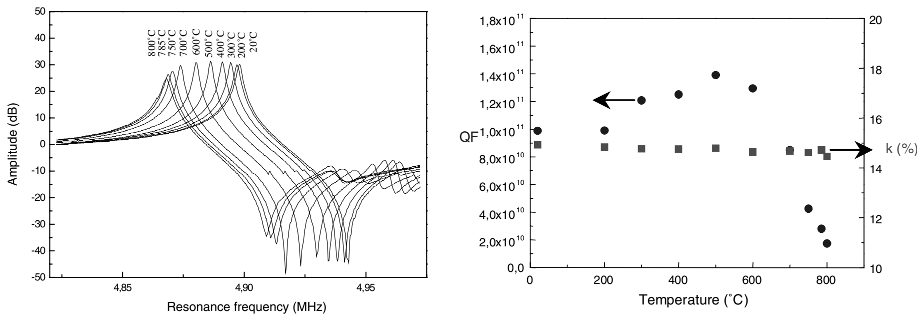

Figure 2. Temperature dependence on the piezoelectric response of a $GaPO_4$ resonator.

The variation of the O-O-O bridging angle distribution as a function of temperature (Fig. 3) obtained from RMC modeling using total neutron scattering data is in good agreement with the piezoelectric measurements. The distribution widens above 700°C and becomes very broad above 850°C due to the dynamical structural disorder. Above 950°C the material transforms irreversibly to the cristobalite phase. In contrast, the intratetrahedral O-O-O angle distribution centered at 60° remains essentially unchanged

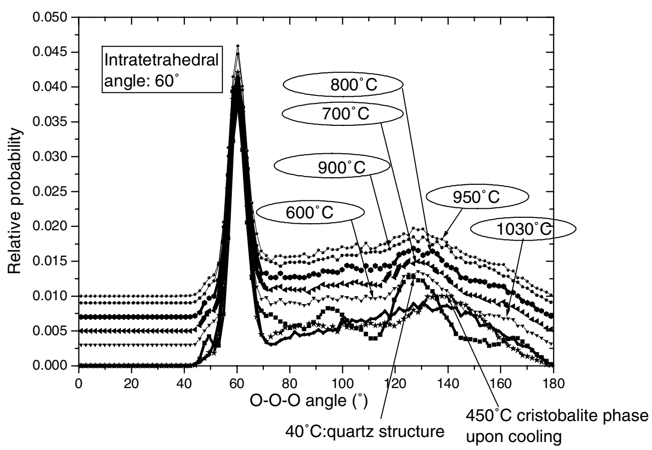

Figure 3. Temperature dependence of the O-O-O angle distribution for $GaPO_4$.

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up to 1030°C confirming that that tetrahedra are essentially rigid units. The relative movement of the rigid tetrahedra can thus be related to the loss in piezoelectric properties well before the phase transition.

4. CONCLUSION

The present study has shown that the degradation of the piezoelectric properties of resonators, in particular the quality factor Q, well below the phase transition can be related to increased structural disorder as characterized by total neutron scattering.

Acknowledgments

The authors are grateful to CMAC and PIEZOCRYST for providing high quality quartz and $GaPO_4$ resonators, respectively. This project is supported by a CNRS/Royal Society cooperation agreement.

References

[1] Philippot E., Goiffon A., Ibanez A. and Pintard M., *J. Solid State Chem.* **110** (1994) 356-362.
[2] Philippot E., Palmier D., Pintard M. and Goiffon A., *J. Solid State Chem.* **123** (1996) 1-13.
[3] Philippot E., Armand P., Yot P., Cambon O., Goiffon A., McIntyre G.J. and Bordet P., *J. Solid State Chem.* **146** (1999) 114-123.
[4] Haines J., Chateau C., Léger J. M. and Marchand R., *Ann. Chim. Sci. Mater.* **26** (2001) 209-216.
[5] Haines J., Cambon O., Philippot E., Chapon L. and Hull S., *J. Solid State Chem.* **166** (2002) 434-441.
[6] Kihara K., *Eur. J. Mineral.* **2** (1990) 63-77.
[7] Young R. A., *Defence Documentation Centre. rep. No. AD 276 235*, (Washington 25, DC 1962).
[8] Goiffon A., Bayle G., Astier R., Jumas J. C., Maurin M. and Philippot E., *Rev. Chim. Minér.* **20** (1983) 338-350.
[9] Shafer E. C. and Roy R., *J. Am. Ceram. Soc*. **39** (1956) 330-336.
[10] Haines J., Cambon O., Keen D. A., Tucker M. G. and Dove M. T., *Appl. Phys. Lett.* **81** (2002) 2968-2970.
[11] Larson A. C. and Von Dreele R. B., *GSAS: General Structure Analysis System*, (Los Alamos National Laboratory, Los Alamos NM, 1994).
[12] Tucker M. G., Dove M. T. and Keen D. A., *J. Appl. Crystallogr.* **34** (2001) 630-638.
[13] Cady W. G., *Piezoelectricity* (Dover, New York, 1964).
[14] Krempl P. W., Krispel F., and Wallnöffer W., *Ann. Chim. Sci. Mater.* **22** (1997) 623-626.
[15] Cambon O., Haines J., "Structure-piezoelectric property relationships in α-quartz isotypes: design and characterization of high performance piezoelectric materials", 2003 IEEE International Frequency Control Symposium, Tampa, 4-8 may 2003, John R. Vig Ed., pp. 650-653.